

CLAIMS

1. A process for the preparation of a polymerizable dental composition comprising the steps of

(a) preparing a liquid mixture comprising

(i) 1 to 99% w/w of a hybrid monomer component containing at least one hybrid monomer compound having one hydrolysable siloxane group and at least one polymerizable organic moiety, and

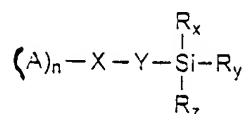
(ii) 99 to 1% w/w of a monomer component polymerizable with the polymerizable organic moiety of the hybrid monomer compounds; and

(b) adding at least a stoichiometrically sufficient amount of water to the mixture to hydrolyse the hydrolysable siloxane group of the hybrid monomer compound and to form spherical polymerizable nanoparticles having an average particle size of from 1 to 100 nm dispersed in the monomer component, whereby the nanoparticles have a structure with Si-O-Si bonds and peripherally exposed polymerizable organic moieties.

2. The process according to claim 1, wherein nanoparticles have an average particle size of from 1 to 20 nm.

3. The process according to claim 1, wherein nanoparticles have an average particle size of from 1 to 5 nm.

4. The process according to claim 1, wherein the hybrid monomer compound is a compound of the following formula (I)



wherein

A is a polymerizable moiety, preferably an acrylate or methacrylate group;

R_x, R_y, R_z

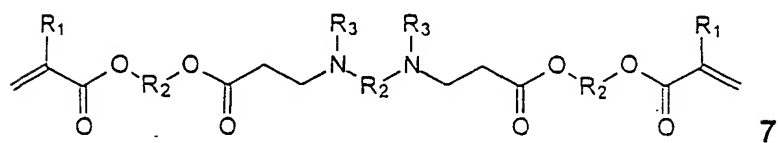
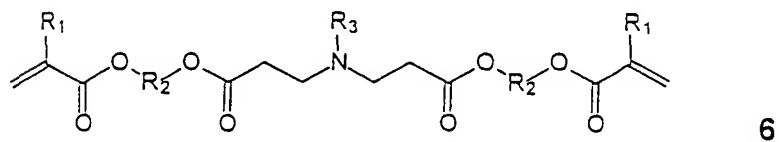
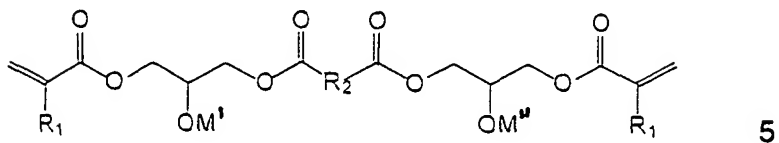
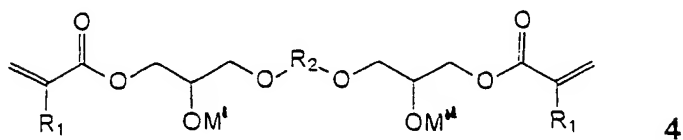
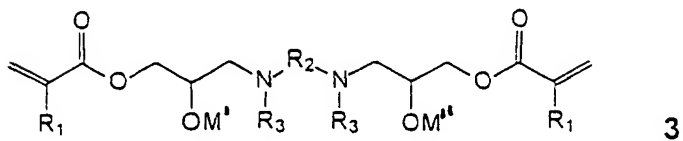
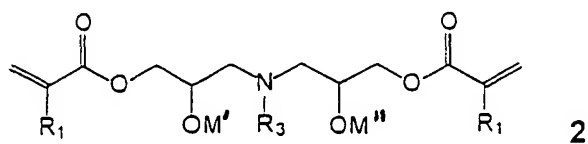
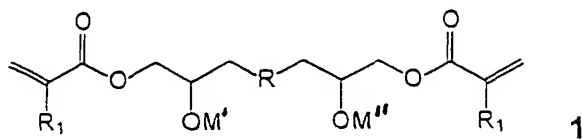
which may be the same or different independently represent substituted or unsubstituted C₁ to C₁₈ alkoxy, C₅ to C₁₈ cycloalkoxy, a C₅ to C₁₅ aryloxy, C₂ to C₁₈ acyloxy or halogen;

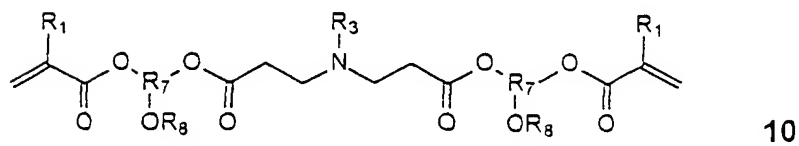
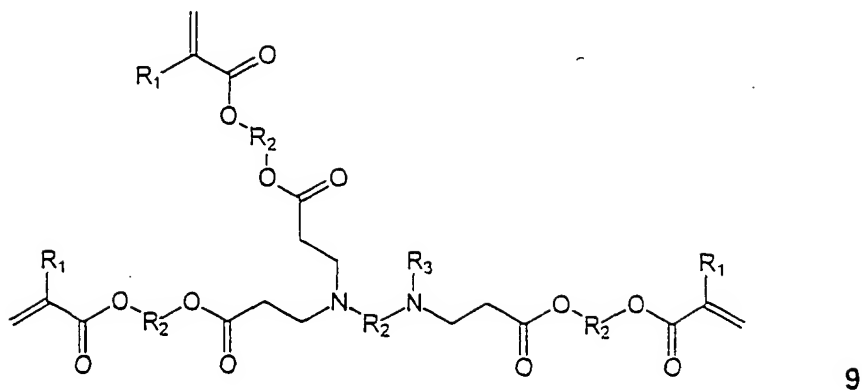
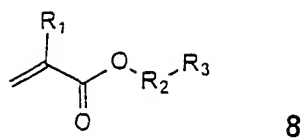
X is a nitrogen atom or a substituted or unsubstituted C₁ to C₁₈ alkylene, C₁ to C₁₈ oxyalkylene or C₁ to C₁₈ carboxyalkylene group;

Y is a substituted or unsubstituted C₁ to C₁₈ alkylene, C₁ to C₁₈ oxyalkylene, C₅ to C₁₈ cycloalkylene, C₅ to C₁₈ oxycycloalkylene, C₅ to C₁₅ arylene, or C₅ to C₁₅ oxyarylene or heteroarylene group; and

n is an integer of 1 to 10.

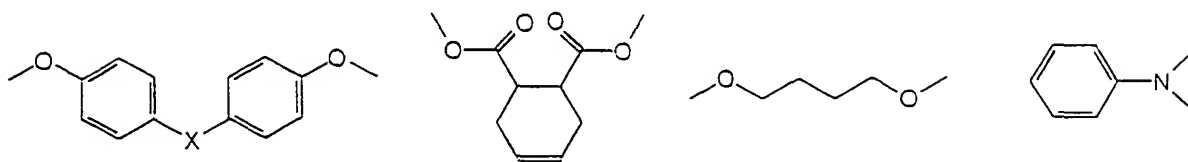
5. The process according to claim 1, wherein the hybrid monomer compound is a compound of the following formulas 1-10:





wherein

R is a residue derived from a diepoxide, notably a residue of the following formula

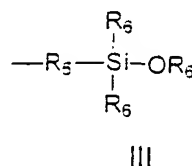
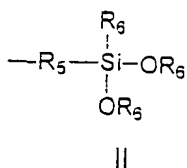
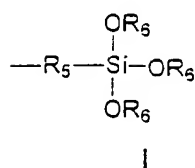


wherein X is C(CH₃)₂, -CH₂-, -O-, -S-, -CO-, or -SO₂-;

R₁ is hydrogen or a substituted or unsubstituted C₁ to C₁₈ alkyl, C₅ to C₁₈ cycloalkyl, C₅ to C₁₈ aryl or heteroaryl group;

R₂ is a divalent substituted or unsubstituted C₁ to C₁₈ alkylene, C₂ to C₁₂ alkenylene, C₅ to C₁₈ cycloalkylene, C₅ to C₁₈ arylene or heteroarylene,

R₃ which may represent the same or different substituents in formula 3 and 7, is a substituted or unsubstituted C₁ to C₁₈ alkyl, C₂ to C₁₂ alkenyl, C₅ to C₁₈ cycloalkyl, C₆ to C₁₂ aryl or C₇ to C₁₂ aralkyl group, or a siloxane moiety represented by one of the following formulae I, II or III



wherein

R₅ is a divalent substituted or unsubstituted C₁ to C₁₈ alkylene, C₂ to C₁₂ alkenylene, C₅ to C₁₈ cycloalkylene, C₅ to C₁₈ arylene or heteroarylene group, preferably CH₂CH₂CH₂,

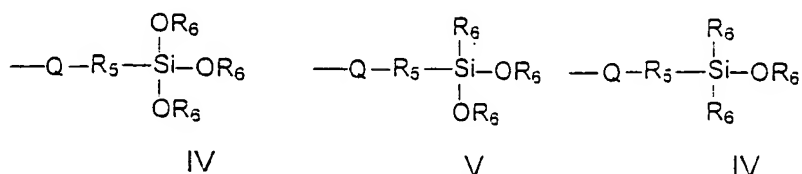
R₆ is a substituted or unsubstituted C₁ to C₁₈ alkyl, C₂ to C₁₂ alkenyl, C₅ to C₁₈ cycloalkyl, C₆ to C₁₂ aryl or C₇ to C₁₂ aralkyl group,

R₇ is a substituted or unsubstituted C₁ to C₁₈ alkylene, C₂ to C₁₂ alkenyl, C₅ to C₁₈ cycloalkylene, C₅ to C₁₈ arylene or heteroarylene group,

R₈ is a protecting group for a hydroxyl group, preferably forming an ether, an ester or an urethane group,

M' and M''

which may represent the same or different substituents, is a siloxane moiety represented by one of the following formulae IV, V or VI, a protecting group for a hydroxyl group, preferably forming an ether, an ester or an urethane group, or hydrogen in case R₃ is a siloxane moiety represented by one of formulae I, II, or III as defined above,

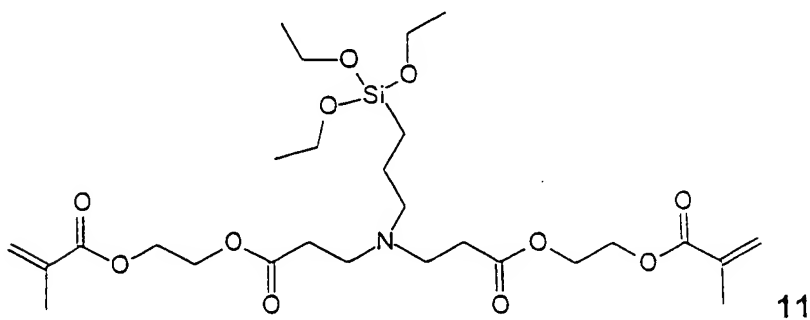


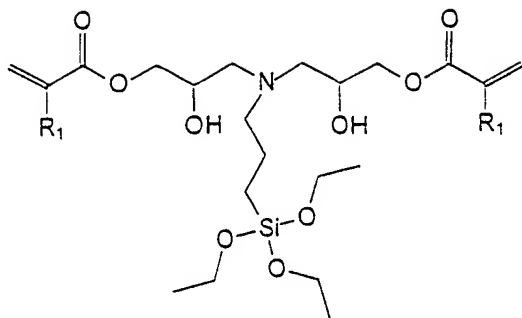
wherein

Q is an ether, an ester, a urethane or thiourethane linking group, and

R₅ and R₆ are as defined above.

6. The process according to claim 1, wherein the hybrid monomer component comprises a compound of the following formula 11 or 12:





12

7. The process according to claim 1, wherein said polymerizable monomer is a mono- or polyfunctional acrylate or methacrylate, selected from the group of methyl methacrylate, ethyleneglycol dimethacrylate, diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, 3,(4),8,(9)-dimethacryloyloxymethyltricyclodecane, dioxolan bismethacrylate, vinyl-, vinylen- or vinyliden-, acrylic- or methacrylic substituted spiroorthoesters, spiroorthocarbonates or bicycloorthoesters, glycerin trimethacrylate, trimethylol propane triacrylate, furfurylmethacrylate.

8. The process according to claim 1, wherein the nanoparticles are formed in the presence of metal compounds selected from the group of alkoxides or metal complexes such as metal acetyl acetonates whereby the metals are selected from the group of Ba, Al, La, Ti, Zr, Hf, In or other transition elements or elements of the lanthanides or actinides.

9. The process according to claim 1, further comprising the step of adding an inorganic filler selected from La_2O_3 , ZrO_2 , BiPO_4 , CaWO_4 , BaWO_4 , SrF_2 ,

Bi₂O₃, a porous glass or an organic filler, such as polymer granulate, embrittled glass fibres or a combination of organic and/or inorganic fillers or reactive inorganic fillers.

10. The process according to claim 1, further comprising the step of adding a polymerisation initiator and a stabiliser.

11. The process according to claim 1, wherein hydrolysis is carried out in the presence of a catalyst.

12. The process according to claim 12, wherein the catalyst is an acid or base.

13. The process according to claim 1, wherein hydrolysis is carried out under neutral conditions.

14. The process according to claim 1, wherein the composition comprises a polymerizable di- or poly(meth)acrylate, at least a polymerizable monomer, polymerisation initiators and/or sensitisers and stabilisers.

15. The process according to claim 1, wherein hydrolysis is carried out in the presence of an organic solvent such as THF, dioxane, chloroform, toluene, acetone.

16. The process according to claim 1, wherein hydrolysis is carried out in the presence of polymerizable monomers such as methyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, trimethylol propane triacrylate, 3,(4),8,(9)-dimethacryloyloxymethyltricyclo decane, dioxolan bismethacrylate, glycerol trimethacrylate, furfuryl methacrylate.

17. A polymerizable dental composition obtainable according to the process of any one of claim 1.